Significance of graphitic structural features in gold adsorption by carbon

P.L. Sibrell and J.D. Miller

Abstract—*The nature of surface sites for the adsorption of gold from alkaline cyanide solutions has been investigated using samples of synthetic, highly-oriented pyrolytic graphite (HOPG). This HOPG material offers an idealized graphite structure enabling the independent study of the graphitic basal-plane sites and the edges, or defect sites, of the graphitic planes. Radiochemical and X-ray photoelectron spectroscopic experiments independently demonstrated that gold adsorption was much higher on the edges (defects) of the graphite planes than on the planes themselves. These results suggest that site-specific adsorption is prevalent in the adsorption of gold by graphitic carbons (including activated carbon, carbon black and graphite) and that most of the favored sites are at edge defects in the graphite crystal structure.*

Introduction and background

Although activated carbon has been used for some time for gold recovery from cyanide leach pulps, the mechanism by which carbon adsorbs gold is still uncertain. McDougall and Hancock (1980) have prepared a comprehensive literature review in this field up to 1980. It has been established that gold is not reduced to the metallic state on carbon during adsorption from alkaline cyanide solutions, as it is in the acidic chloride system. Also fallen out of favor is a mechanism proposed several years ago (McDougall et al., 1980), involving partial reduction of gold with the formation of gold clusters. Current theories for gold adsorption by activated carbon favor adsorption of the gold cyanide complex without chemical change (Adams and Fleming, 1989; Jones, Klauber and Linge, 1989). Researchers at Mintek, in South Africa, maintain that the adsorption of ion pairs is the predominant mechanism under the conditions prevalent in plant operations, that is, in high-ionic-strength alkaline solutions (Adams and Fleming, 1989). At low ionic strength, they propose that ion exchange also becomes important for gold adsorption. However, these researchers do not address the question of where on the carbon surface is the gold adsorbed.

Jones et al. (1989) have proposed that the gold cyanide complex is reversibly adsorbed by the hexagonal ring structure of the basal plane of the cryptocrystalline graphite crystallites present in activated carbon. X-ray photoelectron spectroscopy (XPS) experiments indicated that the nitrogen atoms of the adsorbed gold cyanide complex had identical chemical environments. These researchers interpreted this to mean that no interactions with surface, oxygen-containing functional groups could be taking place. Bonding between the adsorbed gold atom and the π electrons of the graphite ring structure was postulated on the basis of a shift in the binding energy of the adsorbed gold. In essence, the mechanism proposed by Jones et al. (1989) is adsorption without chemical change, which is somewhat in agreement with the Mintek results. However, the Jones et al. XPS data do not support the formation of ion pairs. It may be that the surface state of the adsorbed gold cyanide was altered by the drying and high vacuum required for the XPS procedure.

Using Mössbauer spectroscopy, Cashion et al. (1988) found no evidence for the presence of AuCN or metallic gold on loaded carbon. In contrast to Jones, they proposed that bonding occurs via the nitrogen atoms in the gold cyanide complex, rather than the gold atom.

In another XPS investigation by Cook et al. (1989), experimental evidence was reported for the presence of AuCN on loaded carbon. However, this was probably due to the composition of the solution that was contacted with the carbon. The solution pH was low, around pH 5, where $HAu(CN)_2$ is stable. Furthermore, there is some evidence that when $HAu(CN)_2$ is adsorbed at high loadings, AuCN is formed.

Although it is evident from the above that there is no consensus on the precise mechanism for gold adsorption from alkaline cyanide solutions, recent experimental results seem to support adsorption of the gold cyanide complex without chemical change. However, the nature of the adsorption site on the carbon has not been investigated in great detail, and information in this area may be helpful in determining the adsorption mechanism.

In a research study supported by Newmont (Miller and Sibrell, 1991), gold adsorption by different carbon types was investigated. It was shown that gold adsorption densities are very similar on graphite (Cerac, 4 m^2/g), carbon black (Monarch 800, 200 m^2/g) and activated carbon (NACAR G 204, 1000 m^2/g). However, gold adsorption by diamond (Aesar, 10 m^2/g) could not be detected. These results suggest that the graphitic structure common to the first three materials is responsible for gold adsorption. As is well known, the structure of graphite is very anisotropic, consisting of sheets of covalently-bonded carbon atoms held loosely together by van der Waals forces. Therefore, the question arises of whether gold adsorption takes place predominantly on the basal planes or the edges of the graphite sheets.

Since most forms of graphitic carbon (such as graphite, carbon black or activated carbon) have a complex random arrangement of basal and edge plane structures; it is difficult

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to isolate these areas. However, a much more ideal graphite surface is presented by a synthetic material termed highly-oriented pyrolytic graphite (HOPG). HOPG is manufactured in the US by the Advanced Ceramics Division of Union Carbide. This material is produced by pyrolytic decomposition of methane onto a carbon substrate, followed by high-temperature, high-pressure annealing that brings the graphite layers into very close alignment, almost like a single crystal. However, it should be emphasized that this material is polycrystalline, as revealed by X-ray diffraction measurements. The production and uses of HOPG are further detailed in a review by Moore (1973). HOPG presents an almost defect-free basal plane and, when turned 90°, an almost perfect array of basal plane edges.

In an earlier work, Sibrell and Miller (1991) used a variety of experimental techniques in an effort to detect adsorbed gold on a variety of carbonaceous materials. This proved to be rather challenging, as neither FTIR spectroscopy, with a variety of sampling methods, nor electrochemical methods were sensitive enough to detect adsorbed gold. However, radiolabeling methods and, subsequently, X-ray photoelectron spectroscopy were found to be sufficiently sensitive to detect adsorbed gold. In this contribution, these two experimental techniques were utilized to measure adsorbed gold at HOPG surfaces. The results clearly demonstrate the significance of the graphitic structure in gold adsorption by carbon.

Experimental

Radiochemistry

In this approach, the carbon in the $Au(CN)_2^-$ complex was labeled with carbon-14, and the resultant beta radiation was counted with a proportional counter. The labeled gold-cyanide complex was prepared by the dissolution of metallic gold in a labeled potassium-cyanide solution. The potassium cyanide was labeled with the carbon-14 isotope, which emits beta radiation with a maximum energy of 0.155 MeV and has a half life of 5730 years (Eisenbud, 1987). The tagged potassium cyanide, obtained from the Sigma Corporation, had an activity of 54.4 Curies (Ci) per mole. (One Ci of a radioactive material undergoes 2.22×10^{12} disintegrations per minute (dpm)). The radiolabeled potassium cyanide was dissolved in a small volume of water that had previously been adjusted to pH 10 with sodium hydroxide. Metallic gold (Alfa Products, 99.99%) was added to the solution at double the stoichiometric amount to ensure that all of the cyanide was bound as gold cyanide. Aliquots of this solution were evaporated to dryness in counting planchets for preparation of a calibration curve for the counter.

Fresh basal-plane HOPG surfaces were prepared by removing the top basal plane layer with transparent tape. Edge surfaces were prepared by polishing with fine-grained alumina suspensions on a rotating polishing wheel. The HOPG samples were then exposed to the radiolabeled gold cyanide solution overnight, rinsed thoroughly, dried and placed in a planchet for counting. The radiation was counted with a Canberra gas-flow proportional detector, with an anticoincidence circuit to reduce the background count rate.

An additional radiochemical analysis method for the HOPG samples was by autoradiography, or exposure of photographic film to radiation from the adsorbed, radiolabeled gold cyanide. This method does not give quantitative results, but it is useful for observing the distribution of radiation on the sample surface. Photographic X-ray film, obtained from the Radiology Department at the University of Utah School of Medicine, was exposed to the radiolabeled HOPG samples for various lengths of time and then returned to the Radiology Department for film development. Since the film is more sensitive to visible light than to the emitted radiation, scintillation screens were required to convert the radiation to visible light. Since the carbon-14 isotope emits low-energy radiation, the samples were placed directly in contact with the film, with a scintillation screen below the film.

X-ray photoelectron spectroscopy

In X-ray photoelectron spectroscopy (XPS), a sample is bombarded with X-rays under high-vacuum conditions. This results in the emission of photoelectrons from atoms on the sample surface. This technique is sometimes referred to as electron spectroscopy for chemical analysis (ESCA). Andrade (1985) has published an informative review of the basic principles of XPS. Only photoelectrons released from depths of less than 20 Å to 200 Å from the sample surface can be detected. Consequently, this technique is sensitive only to the composition of the surface material. The electrons are separated on the basis of kinetic energy, and the photoelectron intensity is plotted against binding energy in electron volts (eV). Since each element in the periodic table has a unique set of electron binding energies, the surface elements of the sample can be determined. A concentration ratio of the elements present can also be calculated through the comparison of peak areas, after the use of a correction factor, which takes into account various parameters such as the photoionization cross section of each element. With many elements, a change in the chemical environment causes a slight shift in the binding energy. This allows the determination of the oxidation state of the element and, in many cases, the specific chemical groups present at the sample surface.

Due to charging of the sample, which is more serious with electrically insulating materials, the binding energy values can be shifted by up to 40 eV by the electrical field at the sample surface. Conductive samples, such as graphite, are placed in contact with the instrument ground, a source of electrons. However, even if sample charging is kept to a minimum, a small shift in binding energy can still occur. Therefore, the carbon ls peak is used as an internal standard, and all of the XPS spectra are referenced to it. Unfortunately, different materials are sometimes used for the carbon source, and there is some variation in the binding energy assigned to the carbon ls electron peak. This leads to variations in the measured binding energies, which can then be erroneously attributed to chemical environment effects. Therefore, small shifts in binding energies should be interpreted with caution. Adams (1989) has also discussed this situation. For this investigation, all of the experimentally-determined binding energies were referenced to the carbon ls peak of HOPG at 284.6 eV.

As part of this research, XPS was used to detect the presence of gold cyanide species at both basal plane and edge surfaces of HOPG samples. The HOPG samples were contacted with gold cyanide solutions, rinsed, dried and analyzed at the University of Utah, the University of South Australia and the University of Arizona.

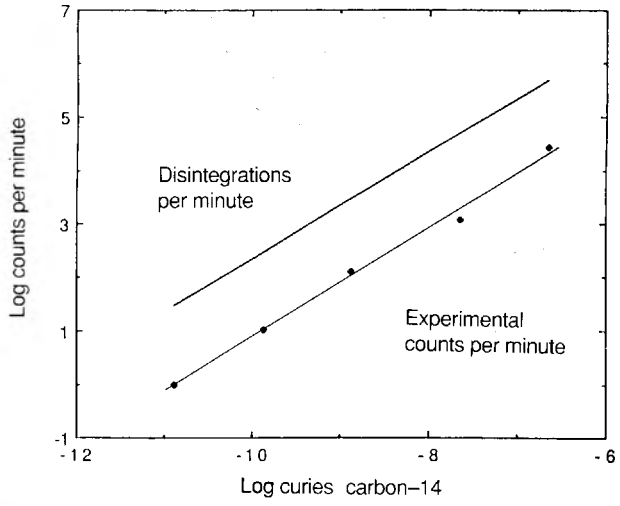


Fig. 1 — Calibration curve for gas-flow proportional radiation counter for analysis of carbon-14-labeled samples.

Results and discussion

Previous research has shown that gold adsorption densities on graphitic materials (based on BET surface areas) averaged on the order of 10^{-11} mole/cm^2 for equilibrium gold concentrations from 1 ppm to 1000 ppm (Miller and Sibrell, 1991). This figure was relatively constant for graphite, carbon black and activated carbon samples. Since these results were calculated from solution depletion experiments and BET surface-area determinations, they reveal little about the adsorption sites on the carbon surface. In this regard, radiochemical methods and XPS spectroscopy have been used to investigate gold adsorption sites at graphite (HOPG) surfaces.

Radiochemistry

The first step in the radiolabeling procedure was the preparation of a calibration curve relating counting rates to the quantity of carbon-14 radiation present in the sample. First, a set of radiolabeled standard solutions was prepared from the radiolabeled, gold-cyanide stock solution. These solutions were also analyzed by liquid scintillation counting to check the carbon-14 concentration. The calibration curve was then prepared by evaporating aliquots of the radiolabeled standard solutions into counting planchets. This resulted in standards containing from 10^{-7} Ci to 10^{-12} Ci.

The calibration curve is shown in Fig. 1. The figure's upper curve shows the disintegration rate of the radiolabeled gold cyanide, as calculated from the radiolabeled solution concentrations. The lower series of points shows the actual count rate detected by the counter. The actual count rate was 3% to 5% of the disintegration rate, due to the inefficiency of the counter and radiation absorption by air, the cellophane covering of the planchet and the counter window. Radiolabeled samples containing 10^{-11} Ci or more of carbon-14 had sufficiently high activities to allow separation from the background counting rate of the detector, which was about two counts per minute. Although the low energy of the carbon-14 radiation led to poor counting efficiencies, this situation also had its advantages. For example, the method was sensitive only to radiation on the sample surface. Any radiation due to carbon-14 that may have penetrated the bulk of the sample would not be detected in significant quantities, due to the attenuation of the radiation by the intervening matter.

Before the actual test work began, the expected activity of the carbon-14-labeled gold cyanide adsorbed at the surfaces of HOPG samples was estimated. As discussed previously, the expected gold cyanide adsorption densities are on the order of 10^{-11} mole/cm^2 of graphite surface. Also, there are two moles of cyanide per mole of gold, according to the stoichiometry of the gold cyanide complex. HOPG samples were prepared with about 1 cm^2 of exposed area. The radiolabeled potassium cyanide used in the preparation of the stock solution had an activity of about 50 Curies per mole. Since one Ci corresponds to 2.22 x 10^{12} disintegrations per minute, a loading of 10^{-11} moles of gold cyanide would be equivalent to 10^{-9} Ci, or an activity of 2220 disintegrations per minute. However, counting efficiencies were on the order of 5%, so the expected count rate should be about 100 counts per minute (cpm), well above the background rate of 2 cpm.

Basal plane and edge samples of HOPG were then contacted with the radiolabeled solution, rinsed, dried and counted. The measured adsorption densities for the basal plane and edge samples were 8 x 10^{-11} mole/cm^2 and 2 x 10^{-9} mole/cm^2, respectively. Since these figures were much higher than expected from solution depletion studies, it was thought that perhaps some gold cyanide salts had been precipitated on the HOPG surface, leading to erroneously-high counting rates. Therefore, the labeled HOPG samples were soaked overnight in deionized water, rinsed thoroughly, dried and counted again. If any gold cyanide salts had been precipitated on the HOPG surface by drying, this procedure should have removed them. The calculated adsorption density decreased, for the basal plane sample, from 8 x 10^{-11} mole/cm^2 to 7 x 10^{-11} mole/cm^2. For the edge sample, this value decreased from 2 x 10^{-9} mole/cm^2 to 1 x 10^{-9} mole/cm^2. Although some decrease was evident, the adsorption densities were still of the same magnitude as before. It is also possible that the observed adsorption-density decreases were due to the stripping of some of the adsorbed gold, due to the soak solution's low ionic strength, rather than the removal of salt crystals.

The radiochemical analysis showed that the gold cyanide adsorption density was much greater on the HOPG edge than on the basal plane. This seems to indicate that the preferred adsorption sites for the gold cyanide complex are at the edges of the graphite planes. These results suggest that site-specific adsorption is prevalent in the adsorption of gold by graphitic carbons (graphite, carbon black and activated carbon), and most of the favored sites are at edge defects in the graphite crystal structure. Other researchers (Adams and Fleming, 1989) have hypothesized that adsorption of the gold cyanide complex is due to ion exchange, under conditions of low ionic strength, and to ion-pair adsorption at high ionic strengths.

It is likely that both of these mechanisms would take place to a greater extent at defects in the carbon structure. Ion exchange would take place where functional groups were attached to the edges of graphitic carbon planes. Although earlier research (Miller and Sibrell, 1991) has indicated that acidic functional groups, as detected by titration, did not correlate with gold adsorption, it may be that the actual functional groups that take part in the ion exchange process are not detected by this technique. For adsorption of ion

Fig. 2 — Scanning electron micrograph (100,000X) of the HOPG basal-plane surface.

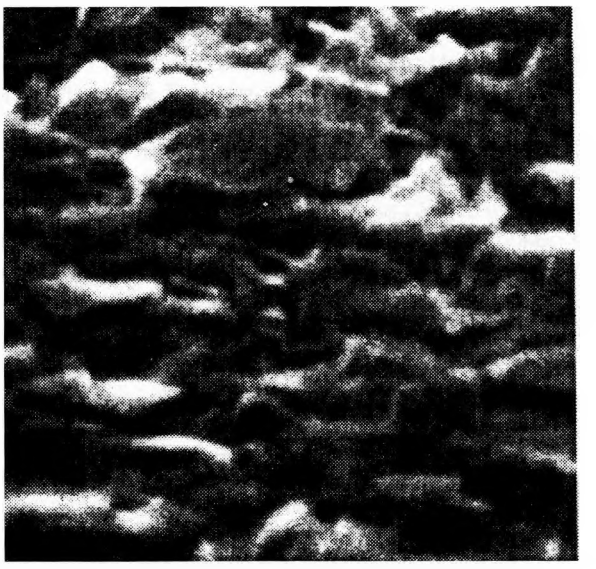


Fig. 3 — Scanning electron micrograph (100,000X) of the HOPG edge surface, after polishing with 1.0-μm alumina grit.

pairs, van der Waals forces would be involved, and the unsymmetrical charge distribution at defects in the graphite structure could well play a role in the adsorption process. It may also be that the adsorbed complex is stabilized by attachment to more than one plane on the carbon, which would not be possible on the flat basal-plane surface. However, this could be more easily achieved at three-dimensional defects in the crystal structure, where edges of the graphitic planes could accommodate or, in effect, "solvate" the ion pair.

The monolayer capacity for the $K^+...Au(CN)_2^-$ ion pair, estimated from the ion pair's size, is found to be roughly 4 x 10^{-10} mole/cm^2, assuming that the ion pair lies flat on the surface and occupies an area of 40 square Å. Using this value for monolayer coverage at the carbon surface, the HOPG basal plane adsorbed 0.2 monolayers, while the HOPG edge adsorbed 8 monolayers. Either multilayer adsorption of gold cyanide is taking place at the HOPG edges, or some other factor is affecting these results. It is possible that the gold-cyanide ion pair does not adsorb flat on the carbon surface. Adsorbing on end would substantially increase the monolayer capacity.

It could be argued that the HOPG edges would be expected to be rougher than the basal plane and, therefore, would show, relatively, a much larger area for adsorption. Therefore, scanning electron micrographs were taken of the HOPG basal plane and the edge surfaces. At high magnification (100,000X), it became evident that the edge surface was indeed much rougher than the basal plane surface (Figs. 2 and 3).

To test the effect of surface roughness on gold adsorption, a second HOPG edge sample was prepared. The first sample had been polished using a 1.0-μm alumina suspension on a polishing wheel. The second sample was polished to a much finer finish, using 1.0-μm, 0.3-μm and 0.05-μm alumina particles in succession. The finer finish of the second sample was confirmed by SEM microscopy (Fig. 4). Although this figure shows a smoother surface for the second specimen, it is still not as smooth as the basal plane sample. When this much smoother HOPG edge sample was counted after the usual adsorption procedure, the adsorption density was found

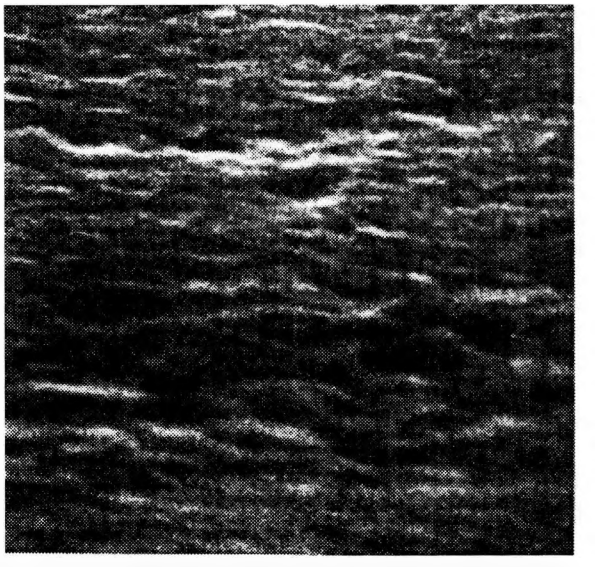
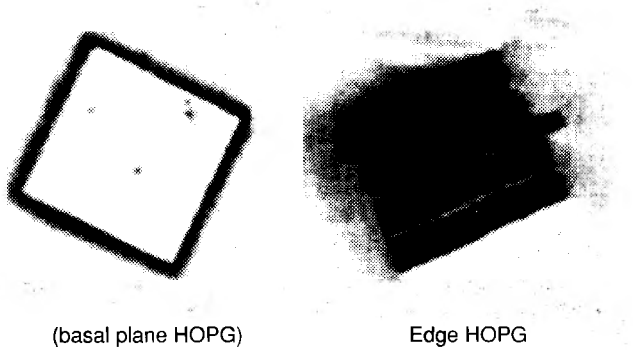


Fig. 4 — Scanning electron micrograph (100,000X) of the HOPG edge surface, after polishing with 0.05-μm alumina grit.

Table 1 — Gold adsorption densities as calculated by carbon-14 radiolabeling.

Sample	Adsorption Density (mole/cm^2) x 10^{10}
Inert materials	
glass	0.3
glass (rinsed)	0.2
silica	0.5
PTFE	0.3
Basal plane HOPG	
after equilibration	0.8
rinsed overnight	0.7
Edge HOPG	
after equilibration	20
rinsed overnight	10
polished	20



(basal plane HOPG) Edge HOPG

Fig. 5 — Autoradiographs of HOPG basal plane and edge samples after contact with radiolabeled gold-cyanide solutions.

to be 2 x 10^{-9} mole/cm^2, essentially the same as that observed for the first HOPG edge sample.

In view of the apparently-high adsorption density found for the HOPG samples, it was decided, at this point, to measure adsorption densities on supposedly inert materials. Thus, for glass, fused silica and polytetrafluoroethylene (PTFE, or Teflon), the resulting calculated adsorption densities were 3 x 10^{-11} mole/cm^2, 5 x 10^{-11} mole/cm^2 and 3 x 10^{-11} mole/cm^2, respectively. These figures all correspond to a sub-monolayer coverage of 10% or less, as would be expected. A tabulation of the measured adsorption densities is given in Table 1.

It is particularly interesting to consider these results in view of previous experimental data. The expected adsorption density of 10 ^{11} mole/cm^2 of total surface area (edges and faces), as calculated from solution depletion experiments for particulate suspensions (Miller and Sibrell, 1991), is much less than that observed for HOPG samples. It may be that the BET area, on which the adsorption densities were based, was overestimated, due to the larger size of the gold cyanide complex when compared to the nitrogen molecule used in BET analysis. If this was indeed the case, the actual area available to the gold cyanide complex would be less than the BET area. Consequently, the actual adsorption densities would be greater than those calculated from solution depletion experiments.

However, it is difficult to believe that the difference of about two orders of magnitude could be explained on this basis alone. One possible explanation for the discrepancy is that in most natural or manmade graphitic carbon samples, the basal plane orientation predominates by as much as a factor of 100. This is due to the lower surface energy of the basal planes as opposed to the edges, which favors the basal plane orientation during crystal growth. In the same way, it is known that basal planes will predominate during breakage of the graphite due to preferential fracture. Since the fracture toughness is much lower parallel to the basal plane than across it (Sakai, Bradt and Fishbach, 1986), most fractures would result in additional basal plane surfaces. Therefore, it is not difficult to imagine that the effective BET area for gold adsorption by carbonaceous materials could be reduced by a factor of 100. In this case, the adsorption density would be 10^{-9} mole/cm^2 for the edge area, which is in good agreement with the radiochemical results for HOPG.

The greater adsorption density on HOPG edge samples was confirmed by autoradiography results (Fig. 5). This illustration shows actual pieces of X-ray film after exposure to HOPG basal plane and edge samples with adsorbed, radiolabeled gold cyanide. Dark areas on the film indicate the presence of radioactivity. The basal plane sample, the light square with the dark border, clearly indicates that most of the radiation is coming from the sample's edges, rather than from the basal plane. This is also evident from the image of the edge HOPG samples, which are uniformly dark.

X-ray photoelectron spectroscopy

Using XPS, other researchers have examined gold adsorption by different activated carbons and have determined binding energies for the gold $4f^{7/2}$ electrons for metallic gold and for $KAu(CN)_2$. Their results are presented in Table 2. Obviously, there is some variability in these results, and this is undoubtedly related to referencing problems, as discussed in the experimental section of this paper. Generally, the binding energy for gold in the metallic state is about 1 eV less than gold in the plus one oxidation state.

The experimental results of the XPS analyses performed in this research are given in Table 3. The binding energies of the gold $4f^{7/2}$ electrons from each sample are given in the first column. These values agree fairly well with results reported by previous investigators and indicate that the gold atoms are in the plus one oxidation state. However, the main thrust of this investigation is the question of whether gold adsorption is greater on the basal plane or at the graphitic edges of the highly-oriented pyrolytic graphite. These results are given in the second column of Table 3. Since XPS is a surface-sensitive technique, only the ratio of gold atoms to carbon atoms on the surface can be calculated. This is not necessarily the same as the adsorption density, and, there-

Table 2 — Published XPS values of gold samples.

Sample	Binding Energy (eV)	Reference
Au metal	84.0	Cook et al., 1989
Au metal	83.0	Andrade, 1985
$KAu(CN)_2$	85.1	Cook et al., 1989
$KAu(CN)_2$	87.1	Adams, 1989
Gold adsorbed on activated carbon from alkaline cyanide solution		
Calgon GRC-22	84.7	Jones, Klauber and Linge, 1989
Norit R2020 and Cabot BP1300	85.8	Cook et al., 1989
LeCarbone G210	85.1	Adams, 1989

Table 3 — Experimental results from the XPS of gold samples.

Sample	Binding Energy (eV)	Ratio Au to C (ppt)
Au metal	83.3	—
Adsorbed $Au(CN)_2^-$		
HOPG edge samples		
Utah - 1000 ppm	85.1	1.4
Arizona - 1000 ppm	85.4	0.9
Arizona - 100 ppm	85.4	0.5
Arizona - 10 ppm	—	ND*
HOPG basal plane samples		
Utah - 1000 ppm	—	ND
Arizona - 1000 ppm	85.6	0.2

* ND = Not Detected

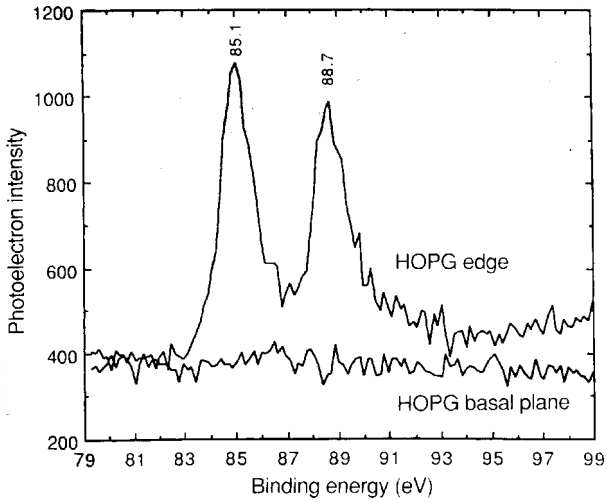


Fig. 6 — X-ray photoelectron spectra in the Au 4f region for HOPG basal plane and edge samples that had been equilibrated with an alkaline cyanide solution containing 1000 ppm gold.

fore, adsorption densities cannot be calculated from these results.

Attempts were made to calibrate the gold loading by sputtering samples of carbon with gold metal for predetermined lengths of time, but the gold-to-carbon ratios were not found to vary significantly with sputtering time. However, for the samples with adsorbed gold, comparisons can still be made between samples based on the gold-to-carbon ratio. At all of the laboratories utilized, gold was detected on the HOPG edge samples by this technique. For samples equilibrated with solutions containing 1000 ppm gold, the ratio of gold to carbon was approximately one to one thousand, or one part per thousand (ppt). This decreased to 0.5 ppt for a sample equilibrated with a solution containing 100 ppm gold, and no gold was detected for the sample equilibrated with a 10-ppm gold solution.

Basal plane samples were equilibrated only with solutions containing 1000 ppm gold. Gold was detected on the basal plane sample only at one of the laboratories, at a level of 0.2 ppt. This may have been below the detection limit of the XPS instrument at the University of Utah, which was an earlier model. However, gold adsorption by the basal plane was not detected for a sample analyzed at the University of South Australia, using a newer XPS system.

These results provide further confirmation of the greater adsorption density of gold at the edges of the HOPG graphite planes than on the basal planes. This is also illustrated by the spectra presented in Fig. 6 for HOPG samples contacted with an alkaline cyanide solution containing 1000 ppm gold. The spectra show electron counts as a function of binding energy, in the region where Au 4f electrons would be detected. The HOPG edge sample clearly shows the presence of gold, by the Au 4f doublet, at 85.1 eV and 88.7 eV, after correction of the carbon Is peak to 284.6 eV. The doublet is due to spin-orbit splitting, which is an effect of the two possible spin states of electrons in p, d and f orbitals. No such peaks were evident for the basal plane sample.

Conclusions

In conclusion, it appears that the adsorption of the gold cyanide complex by graphitic carbonaceous materials is much greater at the edges of graphitic planes than on the planes themselves, although some slight adsorption on the basal plane may occur at high-equilibrium gold concentrations. This conclusion was demonstrated for highly-oriented pyrolitic graphite samples using three different experimental techniques:

- counting of radiolabeled samples,
- autoradiography, and
- X-ray photoelectron spectroscopy.

The greater adsorption density on the HOPG edges does not appear to be related to a greater surface area because of surface roughness, as shown by the comparison between the polished and unpolished HOPG edge samples.

This conclusion is in contrast to that reported by Jones, Klauber and Linge (1989), where adsorption was proposed to take place on basal plane sites. However, the evidence for the hypothesis presented by Jones et al. was not strong and required an imaginative interpretation of the XPS spectral shapes and binding energies. Such an interpretation based on small shifts in binding energies must be questioned in view of the sensitivity of the analysis to the internal standard used for the carbon Is peak.

Also, references were made to the close fit of the gold cyanide complex to the hexagonal ring structure of graphite, yet the size of the cyanide ion in the complex was calculated based on covalent radii of carbon and nitrogen, rather than the ionic radius of cyanide. It has been shown that the cyanide ion is spherical with a radius of 1.92 Å, significantly greater than the sum of the covalent radii of carbon and nitrogen (Cotton and Wilkinson, 1980).

In this research, three different experimental techniques have been used to directly measure gold adsorption densities. Furthermore, these measurements have shown gold adsorption densities to be much greater at the edges of graphite planes. These results suggest that site-specific adsorption is prevalent in the adsorption of gold by graphitic carbons (graphite, carbon black and activated carbon), and most of the favored sites are at edge defects in the graphite crystal structure. Other researchers (McDougall et al., 1980) have hypothesized that the adsorption of the gold cyanide complex is due to ion exchange, under conditions of low ionic strength, and to ion-pair adsorption at high ionic strengths.

It is likely that both of these mechanisms take place to a greater extent at edge defects in the graphite structure. Ion exchange would take place with functional groups that would be attached to the graphitic carbon edges. For adsorption of ion pairs, van der Waals forces would be involved, and the unsymmetrical distribution of charge at edge defects in the graphite structure could well play a role in the adsorption process.

It may also be that the adsorbed complex is stabilized by attachment to more than one plane on the carbon. Although this would not be possible on the flat basal-plane surface, it could be more easily achieved at three-dimensional edge defects in the crystal structure. These cavities created by edges would accommodate or, in effect, "solvate" the ion pair. This important phenomenon has been identified for activated carbon (Adams, McDougall and Hancock, 1987a), for solvent extraction (Wan and Miller, 1986; Miller et al., 1987; Mooiman and Miller, 1991; McDougall, Adams and Hancock, 1987) and for resin adsorption reactions (Akser,

Wan and Miller, 1986; Adams, McDougall and Hancock, 1987).♦

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